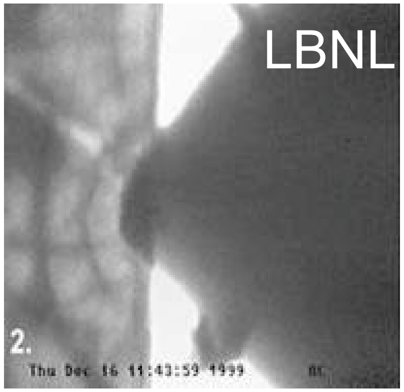
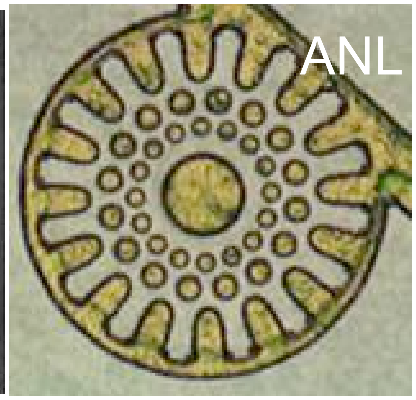
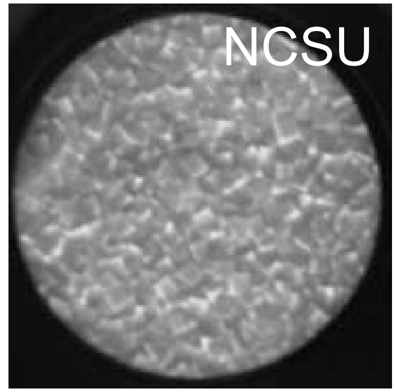


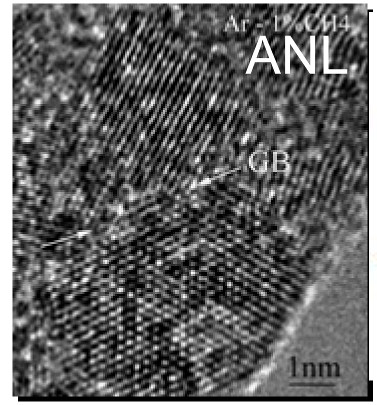
TEM / Nanoindentor



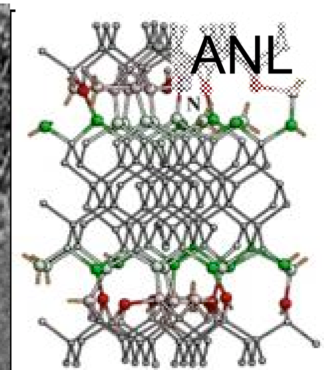
UNCD MEMS



PEEM / FEEM imaging



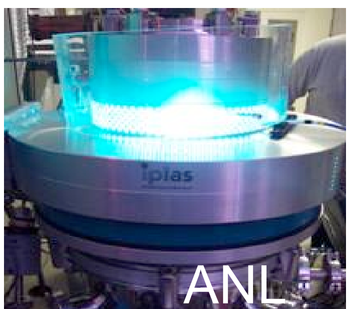
UNCD



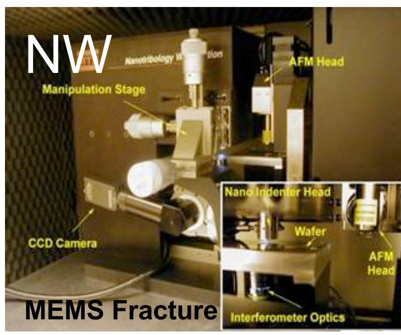
Tight Binding Molecular Dynamics Studies

Carbon-based Nanostructured Materials

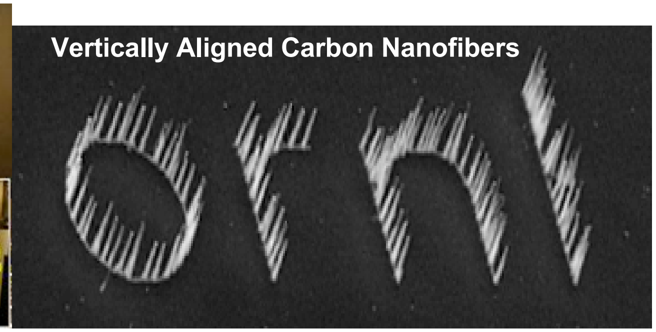
John A. Carlisle, Tom A. Friedmann



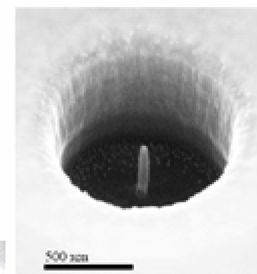
Microwave Plasma CVD

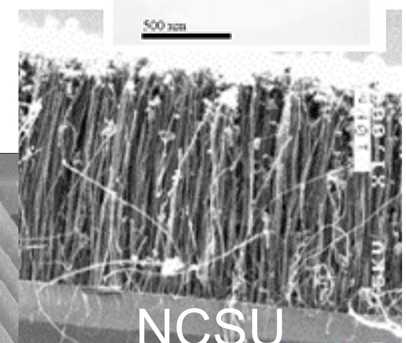


MEMS Fracture

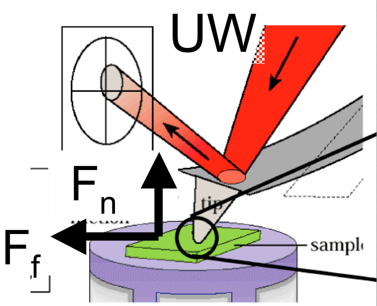


Field Emission

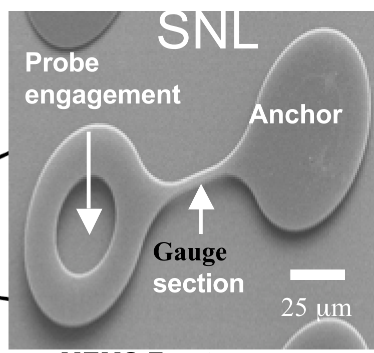




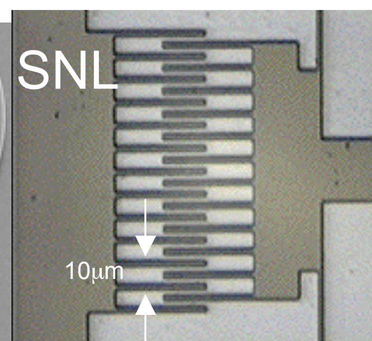
Nanotubes



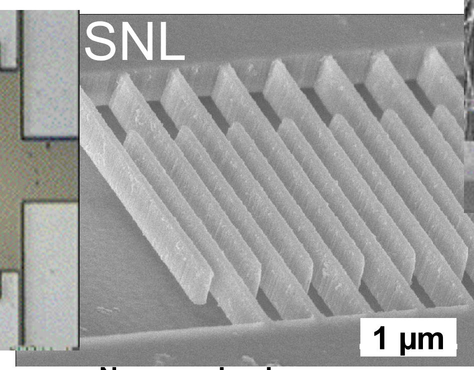
Nanotribology



MEMS Fracture



a-D MEMS



Nanomechanics

Outline

- Introduction/Overview of Project Tasks/Goals, People, Budget
- Research Highlights Summary
- Technology Highlights
- Other Examples of Project Impact (Conferences, NanoCarbon/Nanotubes Themes, Invited Papers, Follow-on funding, etc.)
- Highlight Presentations
  - Functionalized Carbon Materials
  - Fracture Toughness of a-D & UNCD
  - Tribology and Surface Chemistry of UNCD and NFC.
- Summary and Future Work

The Team

Workshop at NCSU – February 23, 2004

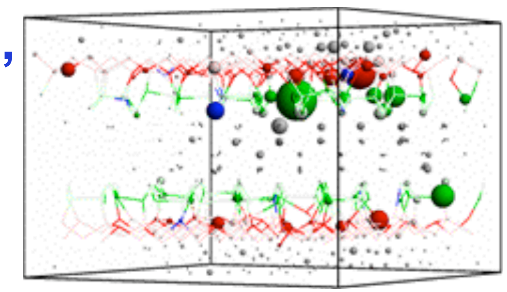
Budget

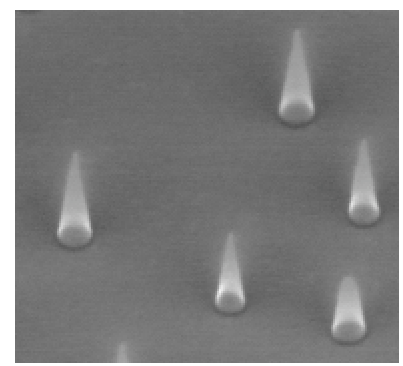
Institution	Funding ($1,000's)	Type of Support
ANL	$55 15	Postdoc Graduate Student (Theory)
SNL	65	PI's
ORNL	65	Postdoc
LBNL	25	Graduate Student
UW-Madison	25	Graduate Student
NCSU	25	Graduate Student
UF	10	Graduate Student
All	15	Annual Workshop (coordinated by ANL/SNL)
TOTAL	$300	

$220K Funding used to support postdocs, graduate students

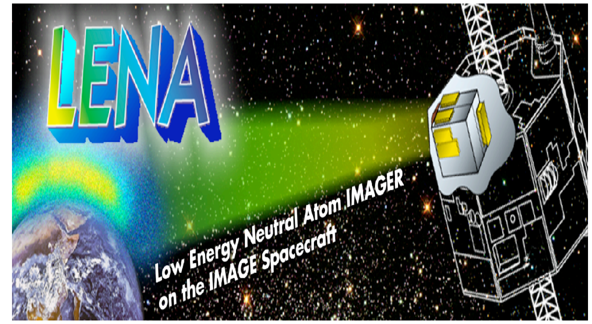
Science Highlights

- Self-Assembled Carbon Nanocomposites & Flying Nanotubes (ANL, ORNL)
- Functionalized Diamond surfaces (ANL, UW-Madison, NCSU)
- Vertically aligned carbon nanofibers/nanocones (ORNL)
- Fracture Toughness of a-D and UNCD (NW, SNL, ANL, UF)
- Quantum Chemistry Simulations of electronic transport in n-type UNCD
- Field Emission/Thermionic Energy Generation (NCSU, ANL)
- Thermal Transport of UNCD (ANL, UF)
- Tribology/Surface Chemistry (including NEXAFS) of a-D, UNCD and NFC (UW-Madison, SNL, ANL)





Technology Highlights



- Conversion Electron Surfaces (SNL/ANL collaboration with NASA/Goddard)
- LBNL/Hysitron Corporation SBIR
- UNCD/IPLAS R&D100 award
- Advanced Diamond Technologies, Inc. (SBIR)
- New large area plasma system at ANL (OIT,OBER)

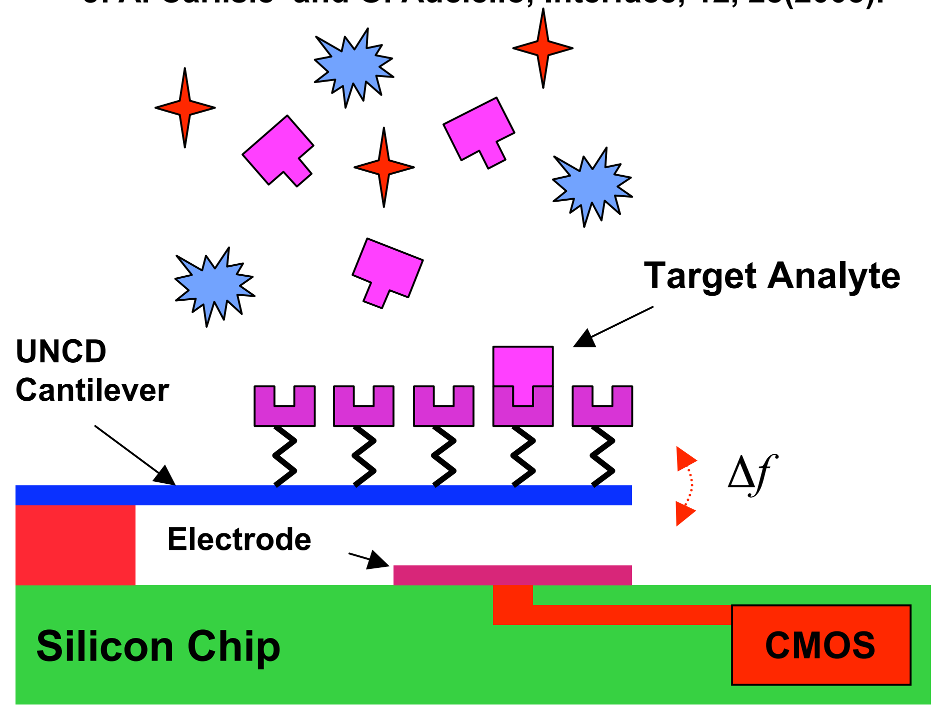
Impact

- **Papers: 10**
- **Invited Presentations: 17**
- **Follow-on Funding:**
  - DARPA, NIRT, LDRD, MURI, SBIR
- **Other Stuff:**
  - ADC/NanoCarbon 2005 Conference at ANL
  - Spring 2005 MRS Symposium on Diamond
  - NanoCarbon Theme at the ANL Center for Nanoscale Materials (upcoming Workshop)
  - Nanotube RFA at the ORNL Center for Nanophase Materials Sciences.
  - Industrial Collaborations

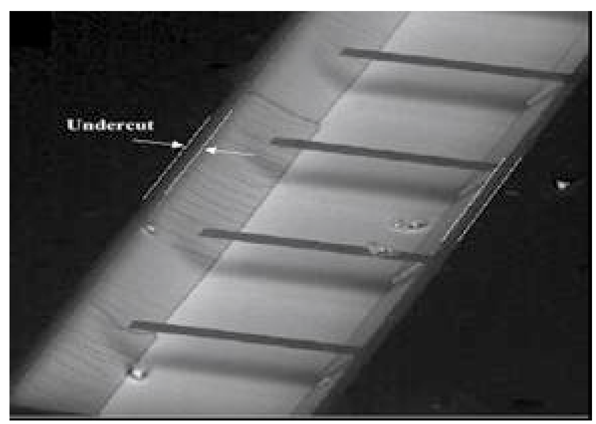
Synopsis: UNCD Could enable robust Biosensors

- Electrochemical Electrode (Wide working potential)
- UNCD can be grown at low temperatures
- UNCD can be made highly electrically conductive
- UNCD Mechanical properties (high frequency, high Q)
- UNCD MEMS
- Bio-inert, Bio-compatible
- Surface Functionalization (Robust, Stable, Selective)

J. A. Carlisle and O. Auciello, Interface, 12, 28(2003).



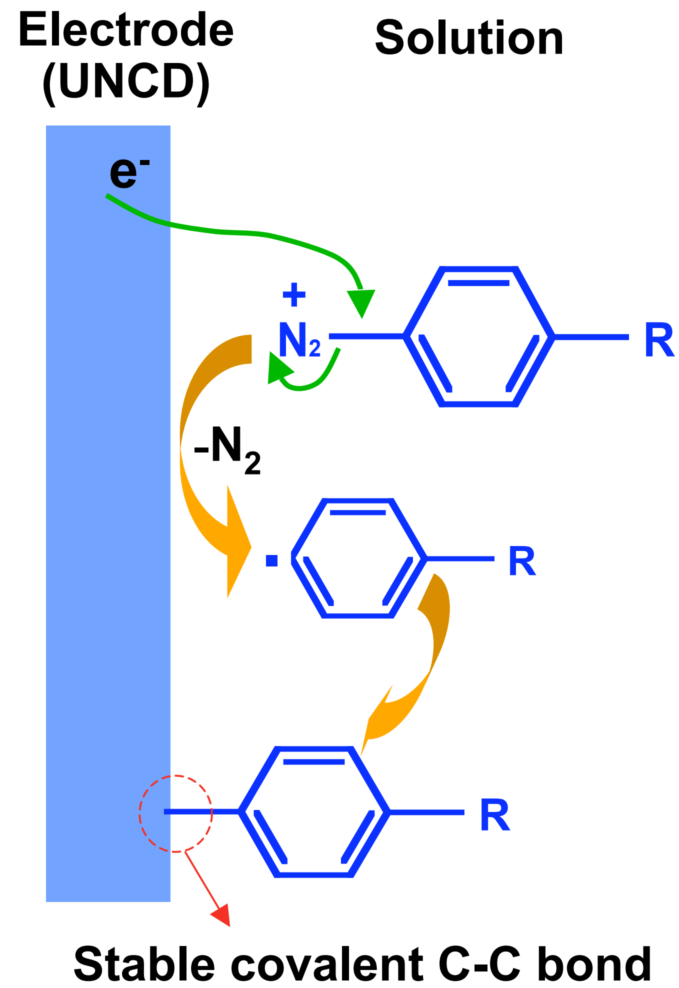
UNCD BioMEMS Sensor



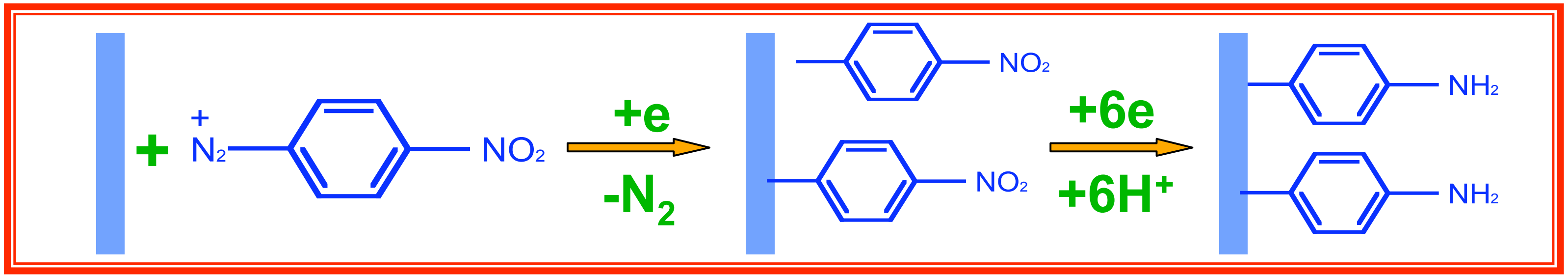
UNCD cantilevers

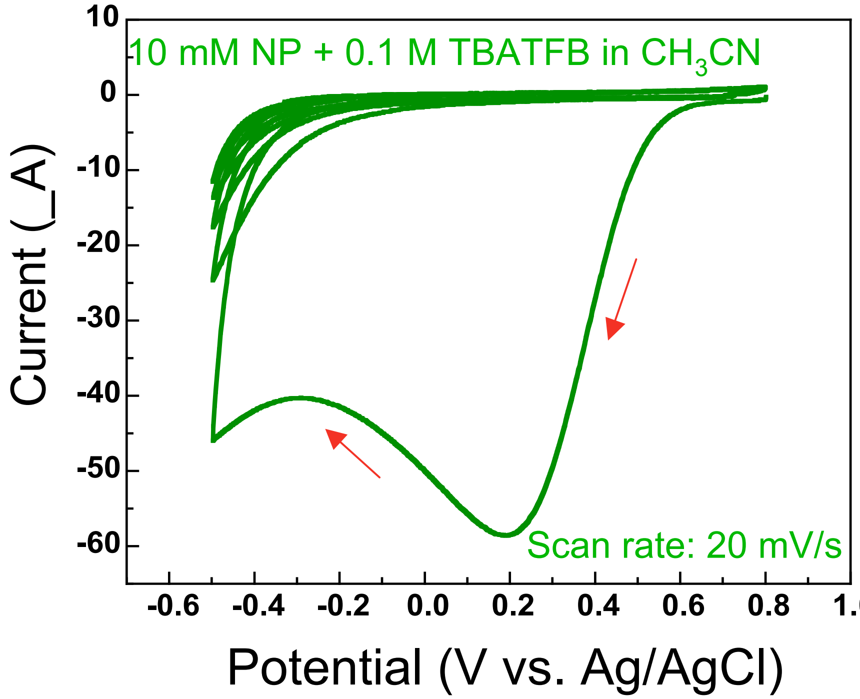
Electrochemical Functionalization of UNCD

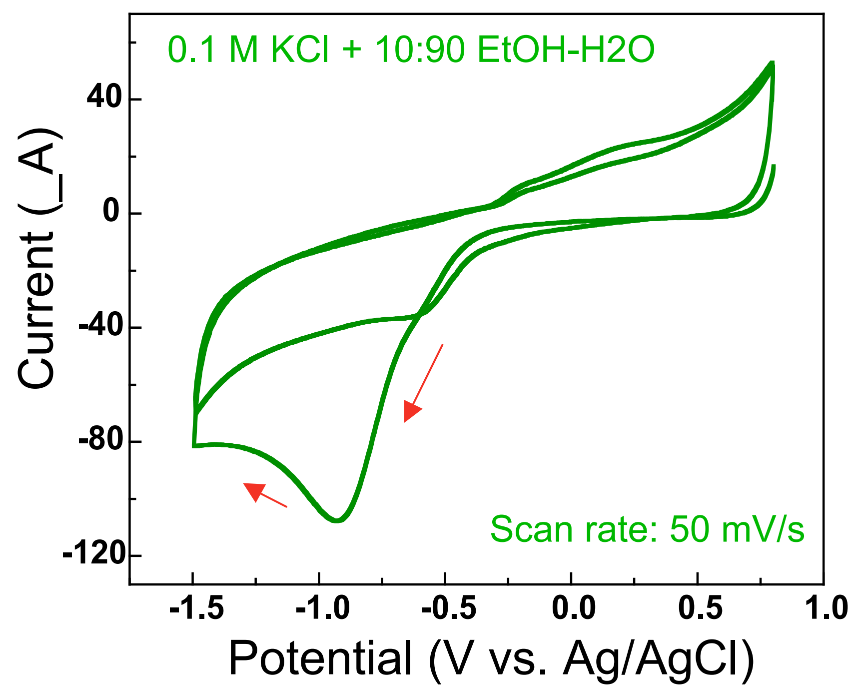
- Radicals generated by electrochemical reduction of aryl diazonium cations
  - One electron transfer reaction
  - Radicals are generated at the electrode/electrolyte interface
  - Radicals couple to UNCD surface forming covalent bonding
- Advantages
  - Simple and fast (in minutes or seconds vs. hours in photochemistry)
  - Negligible bulk reaction
  - Abundant aryl derivatives



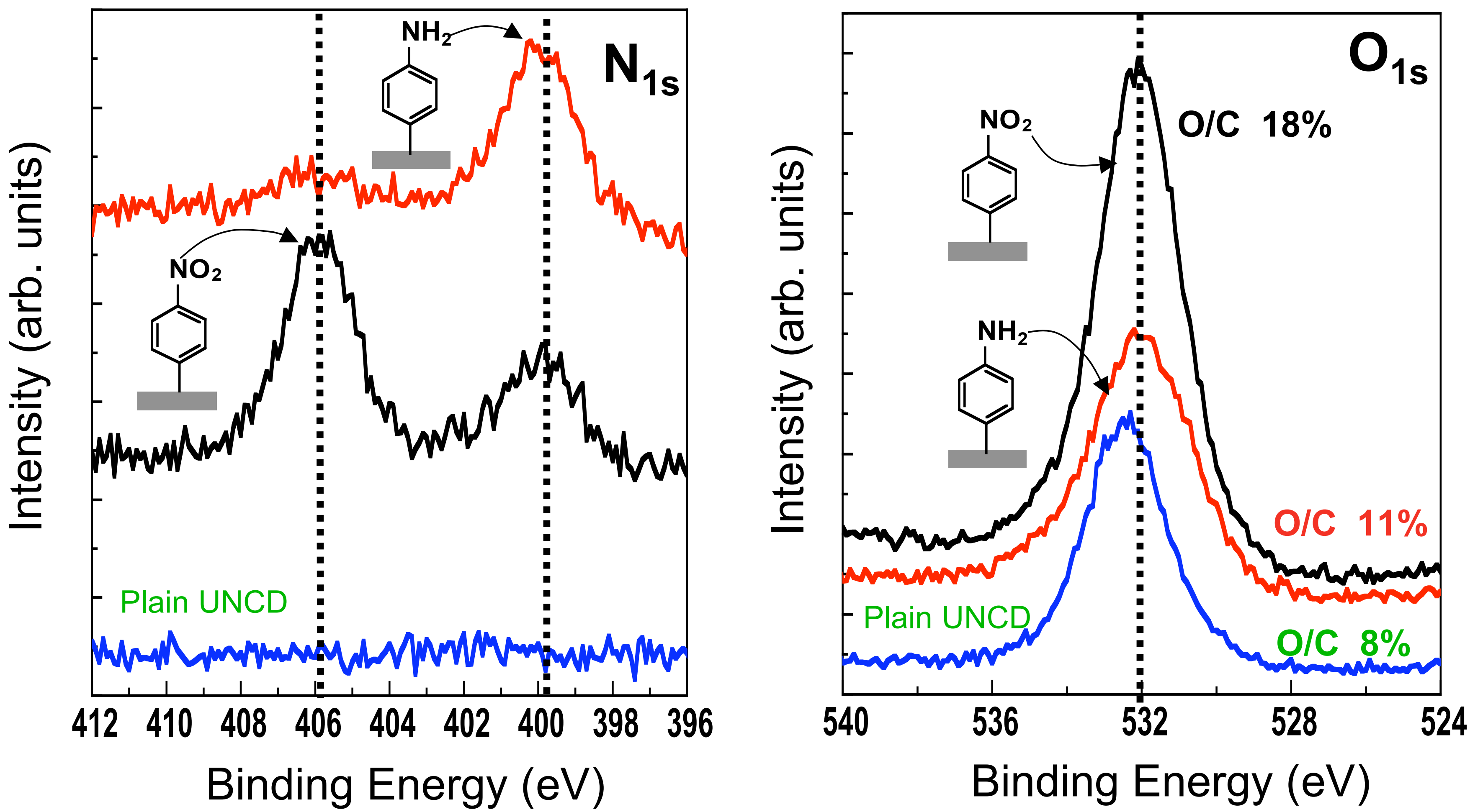
Electrochemical Functionalization of UNCD with 4-Nitrophenyl Diazonium





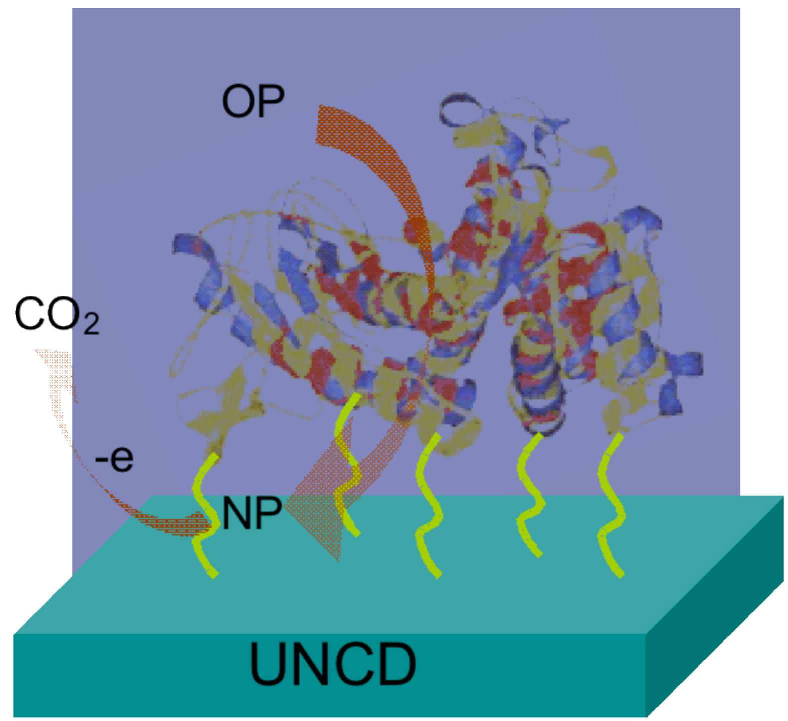


XPS of 4-Nitrophenyl-modified UNCD



Electrochemical Biosensor

- Neurotoxic organophosphates (OPs)
  - chemical warfare agents
    - Iran-Iraq conflict
    - 1995 Tokyo subway incident
- Enzyme-based electrochemical sensing
  - simple, rapid and lightweight
  - truly portable bioanalytical devices
- Integration the UNCD-based biocomposites with electrochemical detection will ultimately yield biosensing devices with enhanced biocompatibility, sensitivity, selectivity and stability.



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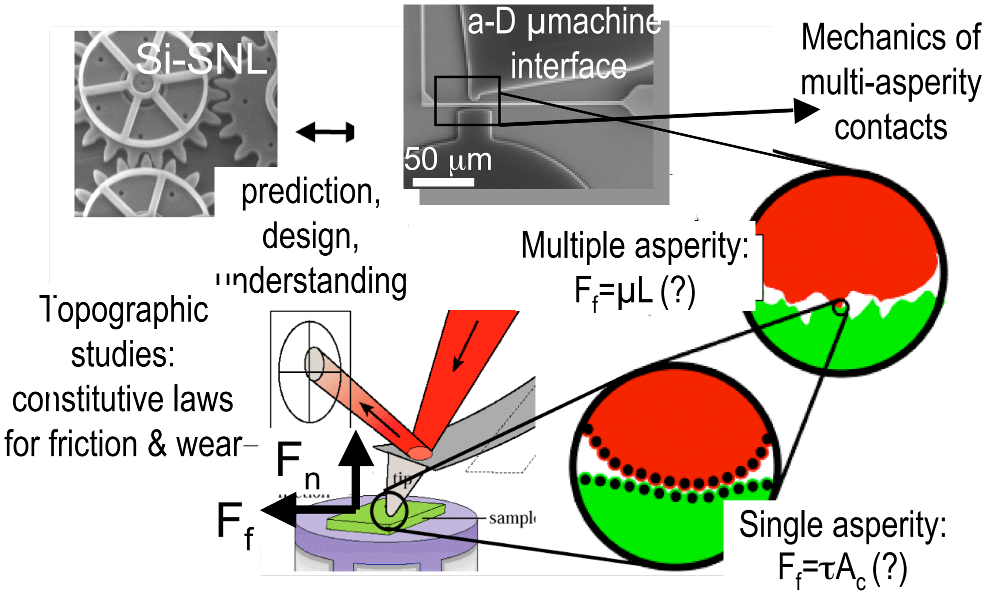
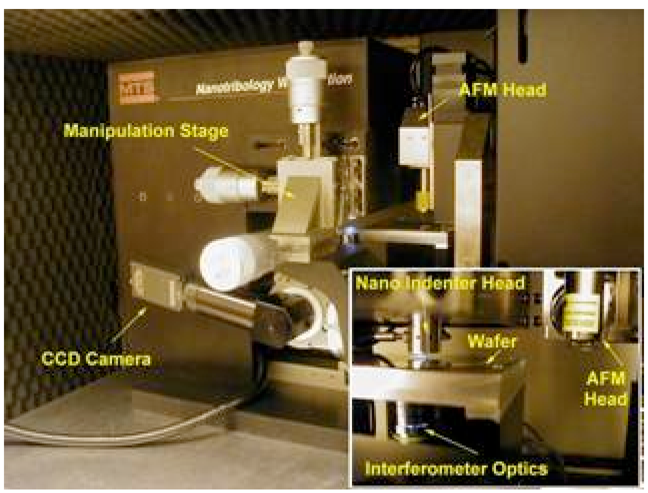
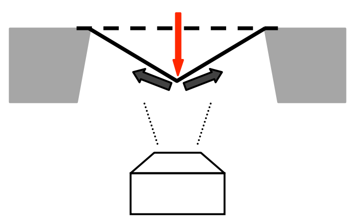
  - **Tribology and Surface Chemistry of UNCD and NFC.**
  - **Fracture Toughness of a-D & UNCD**
- **Summary and Future Work**

Do new tribological and mechanical behaviors emerge in carbon-based materials at the nanoscale?



- **What are the tribological consequences of reduced dimensions?**
  - **Transfer film formation**
  - **Surface chemistry**
  - **Adhesion**
- **What are the mechanical consequences of reduced dimensions?**
  - **Nature of strength limiting defects**
  - **Energy dissipation**
- **Can we demonstrate improved function of carbon based MEMS over their Si counterparts?**





Nanoscale mechanics studies of nanostructured carbon materials and new measurement techniques

Collaboration is the key to progress

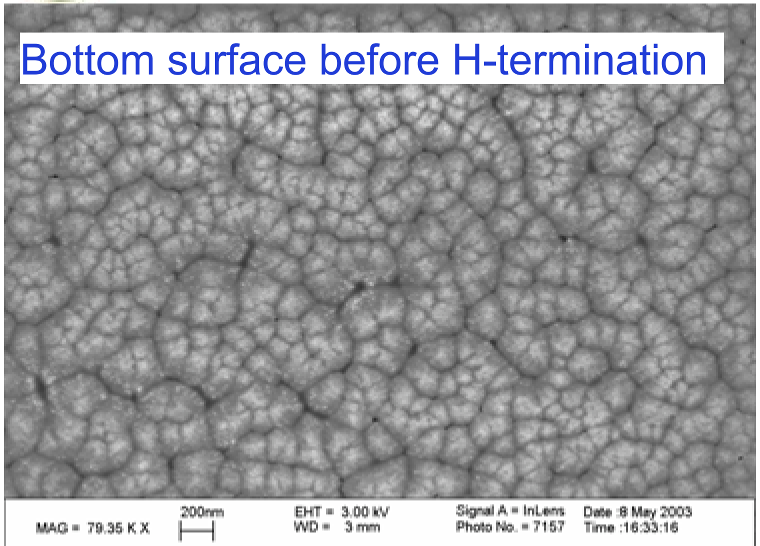
Tribology of carbon at varying length scales

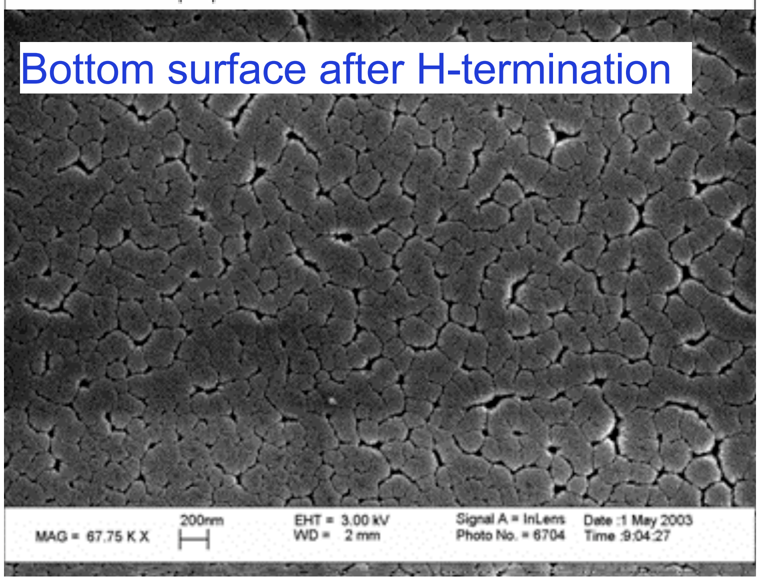
Investigator	Institution	Contributions
M. Dugger	SNL	Micro- and nano-scale tribology
R. W. Carpick	**U. W. Madision**	**AFM based friction/adhesion**
T. A. Friedmann	SNL	a-D growth, characterization, device fab.
J.A. Carlisle	ANL	UNCD growth and characterization

Mechanical properties of carbon based MEMs

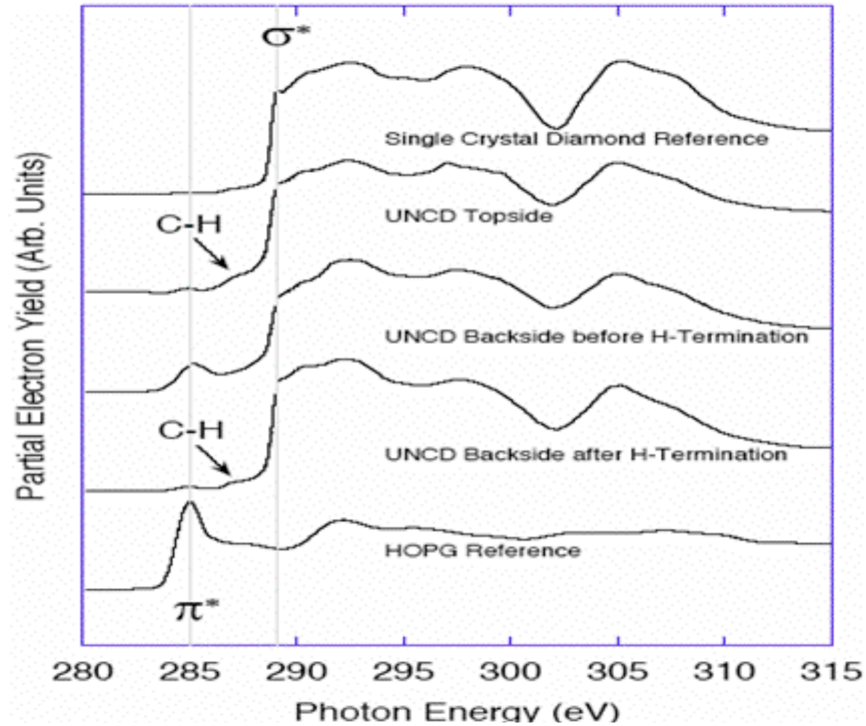
Investigator	Institution	Contributions
T. Buchheit	SNL	Micromechanical testing
H.D. Espinosa	**NW**	**Micromechanical testing with strain**
T. A. Friedmann	SNL	a-D growth, characterization, device fab.
O. Auciello	ANL	UNCD growth and characterization

H-plasma treatment changes UNCD backside bonding and morphology



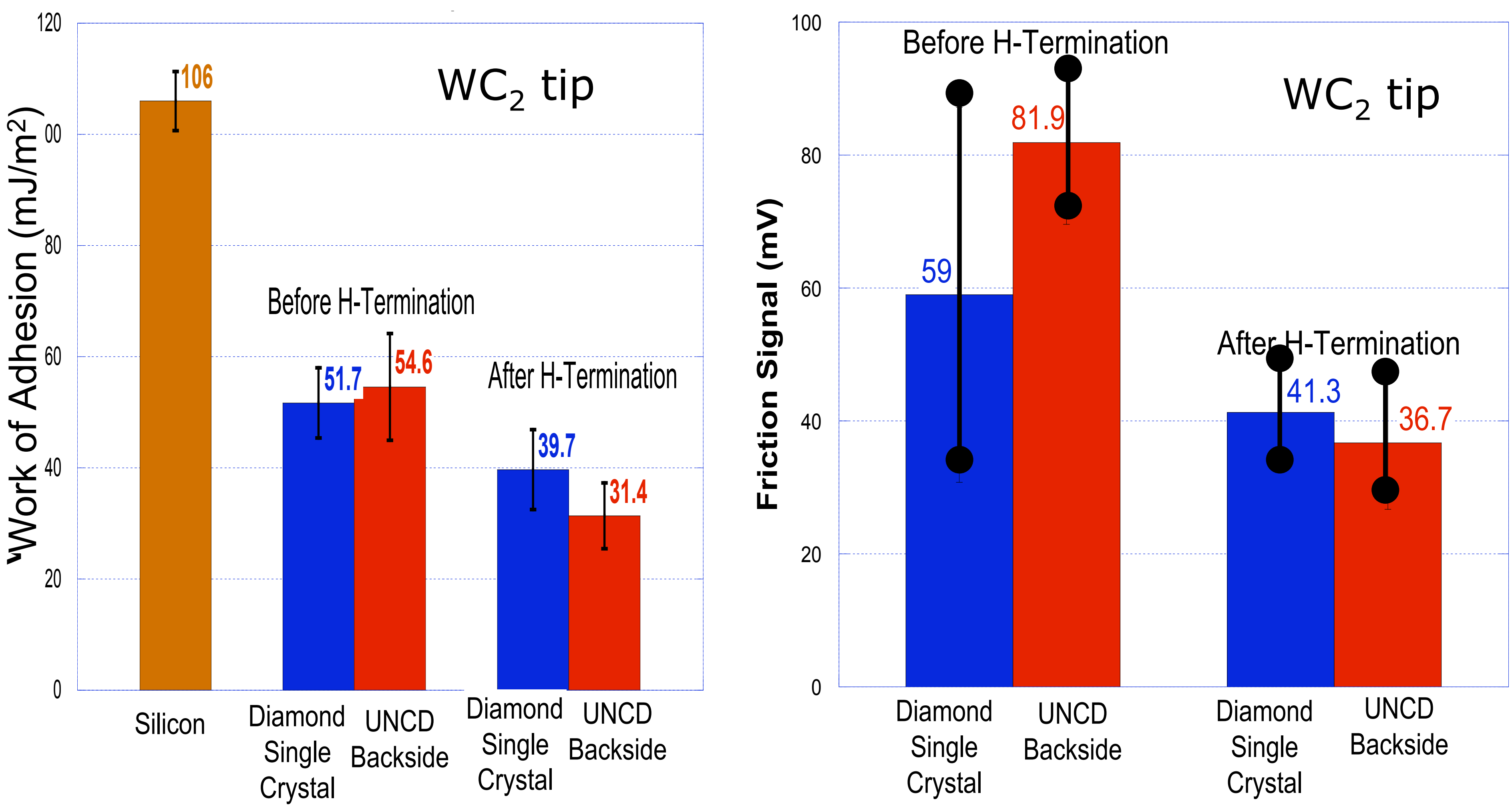


Substrate chemically etched away



- Ultrasonically seeded with diamond nanoparticles
- H appears to etch the super grain boundaries
- Grain boundaries and super grain boundaries may be regions of sp^2- bonded carbon that get etched faster by H.
- NEXAFS confirms removal of sp^2 and H-termination

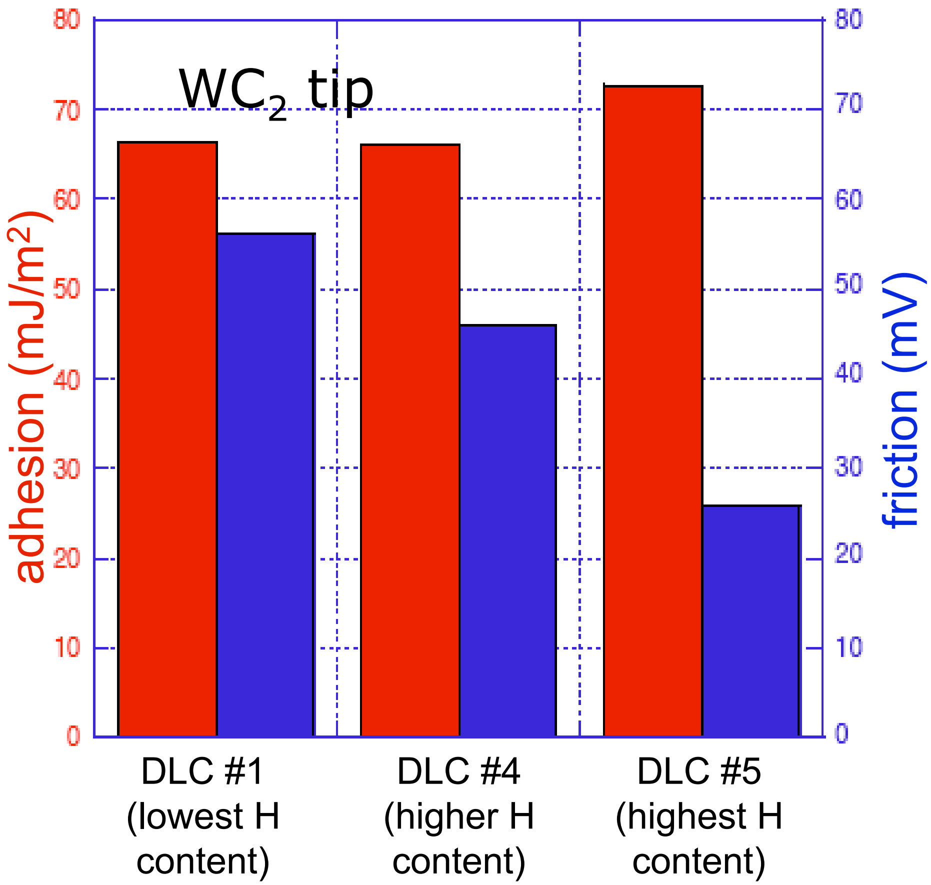
H-Surface termination reduces nanoscale friction and adhesion in diamond



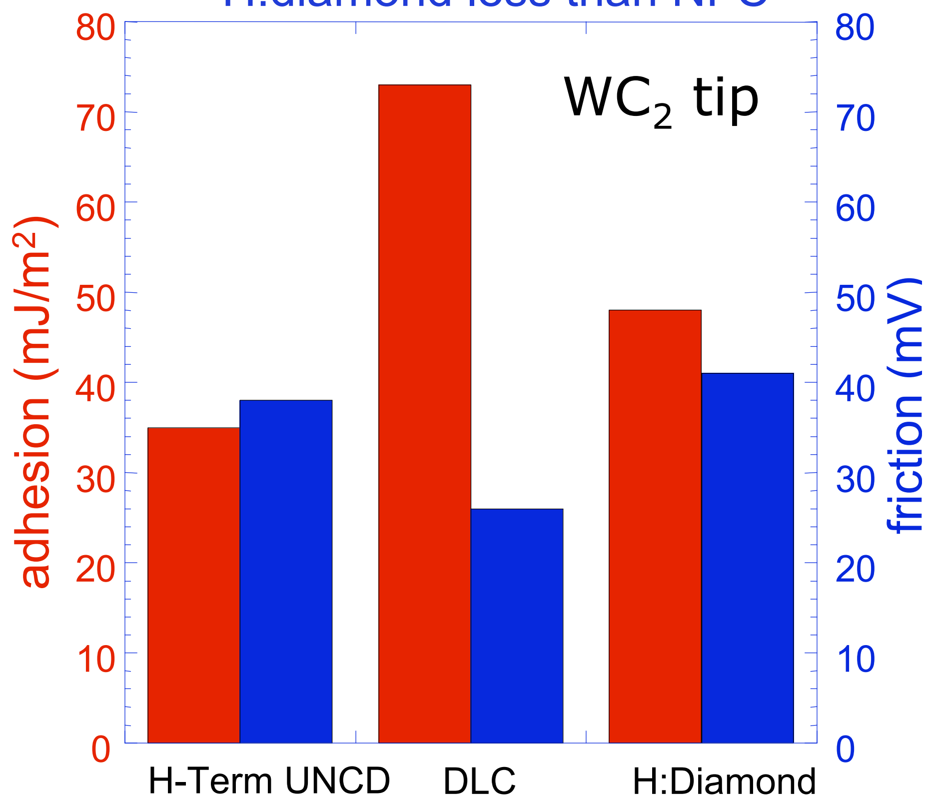
R. Carpick UW-Madison

Comparison of friction and adhesion in NFC and diamond

Friction in NFC decreases with increasing H content - adhesion is constant

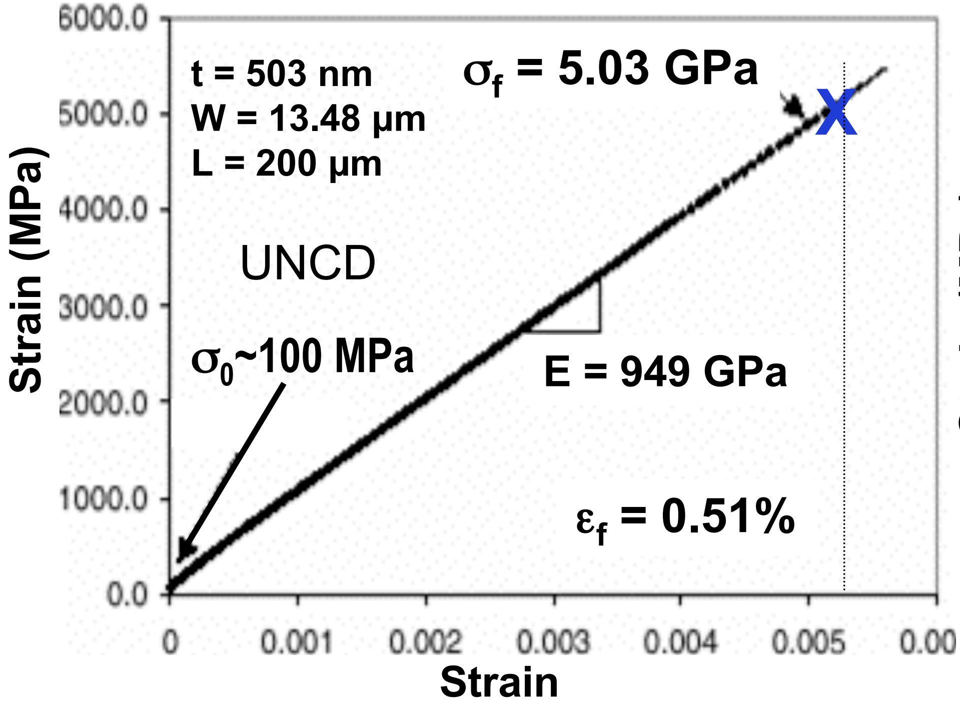


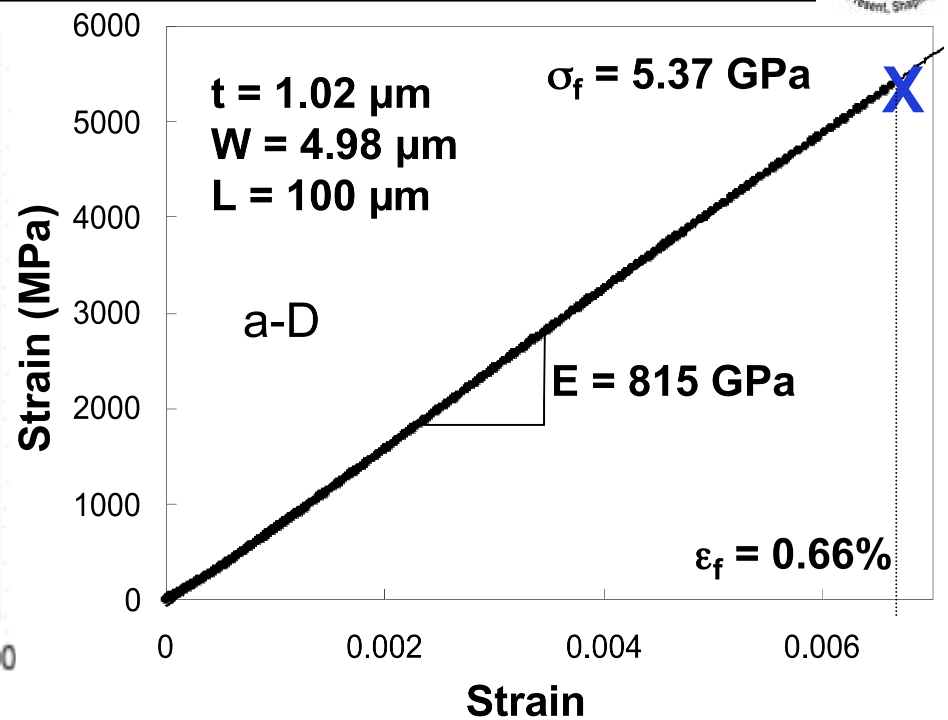
Adhesion in H:UNCD and H:diamond less than NFC

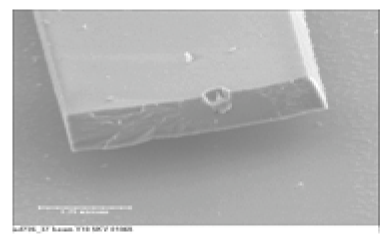


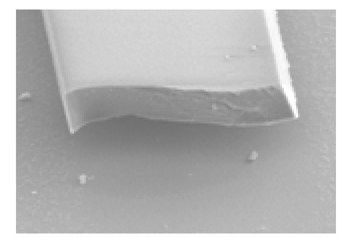
R. Carpick UW-Madison

Fracture behavior of nanostructured materials- A comparison between a-D and UNCD



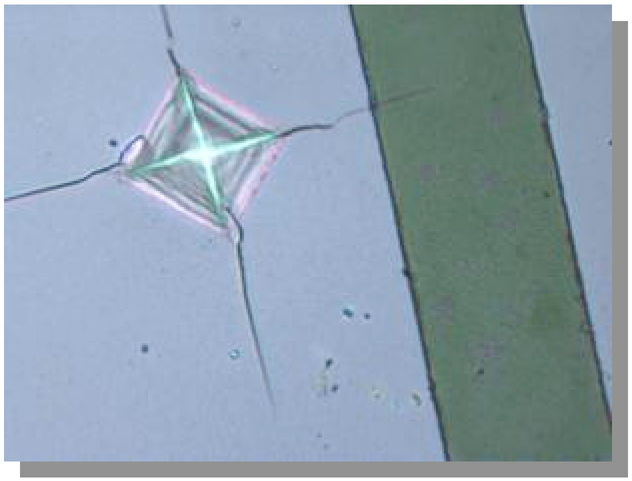


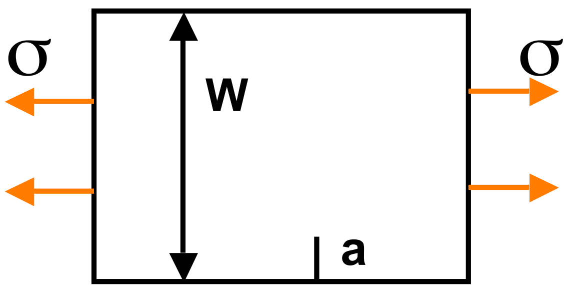




- Low strength samples have flaws from mechanical seeding process. Ultrasonic seeding gives much higher strength
- Low strength samples have flaws due to masking problems. High strength samples fail at sidewall due to etching induced roughness

UNCD and a-D have high fracture toughness





$$K_{IC} = \sigma_f \sqrt{\pi a} f(\frac{a}{W})$$

$$f(\frac{a}{W}) = 1.12 - 0.23(\frac{a}{W}) + 10.55(\frac{a}{W})^2 - 21.72(\frac{a}{W})^3 + 30.41(\frac{a}{W})^4$$

H.D. Espinosa NW

- Microindentor used to induce sharp crack in beam by propagation from the sacrificial material.
- Sharp cracks allow accurate calculation of fracture toughness

UNCD

a (μm)	W (μm)	$\sigma_f^{(exp)}$ [GPa]	K_{IC} [MPa$\sqrt{m}$]
2.1	18.1	1.35	4.1
3.9	18.2	0.95	4.4
5.8	18.0	0.78	4.7
6.6	18.2	0.71	4.5
8.2	18.1	0.70	4.1

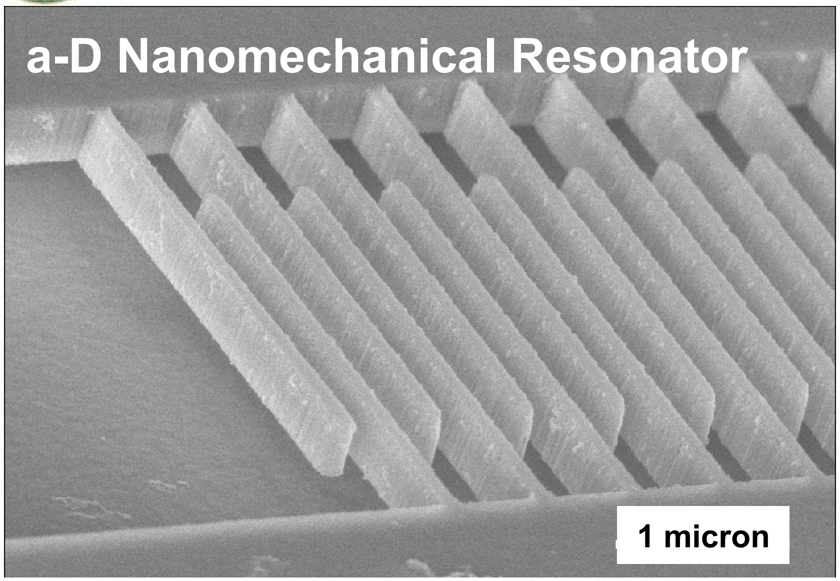
a-D

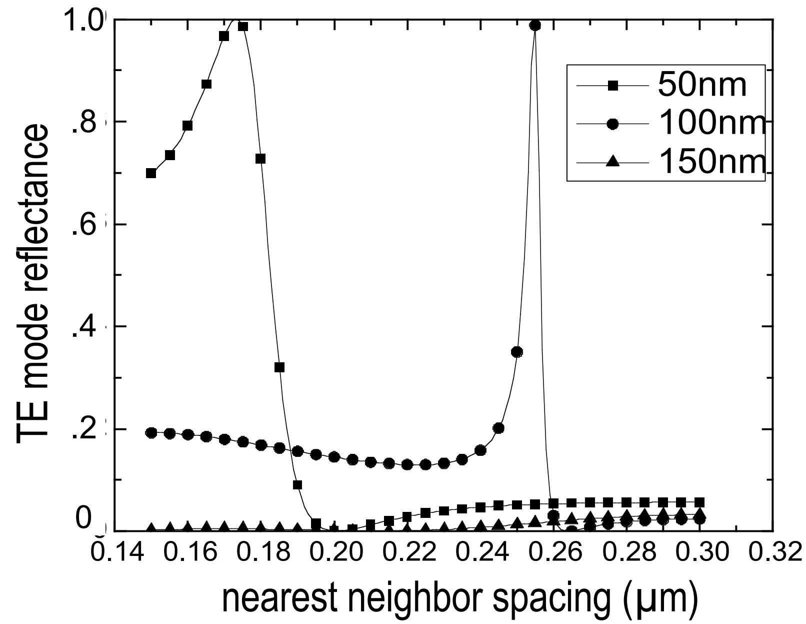
a (μm)	W (μm)	$\sigma_f^{(exp)}$ [GPa]	K_{IC} [MPa$\sqrt{m}$]
3.7	37.2	1.25	5.0
5.5	37.5	1.09	5.6
7.6	37.5	0.77	5.0
10.2	37.3	0.62	4.9
12.8	37.1	0.58	5.2

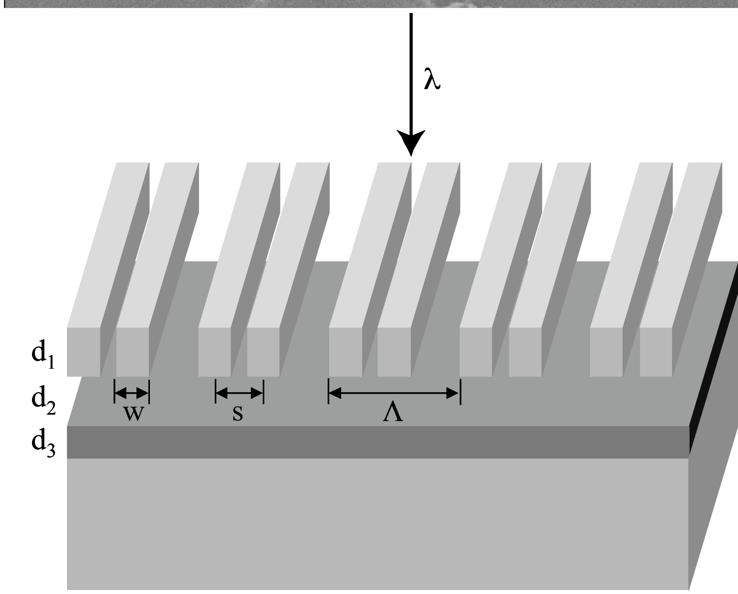
Summary of fracture behavior

Material	E (GPa)	K_{1C} (MPam$^{1/2}$)	σ_{0V} (MPaμm$^{3/m}$)	Weibull Modulus	$\sigma_x(d_0)$ (Gpa)	d_0 (nm)
UNCD	955	4.5	8581	11.6	18	35
a-D	800	6.2	8622	13.5	25	38
polysilicon	160	1		9		15

Laterally deformable nanomechanical motion sensor with high sensitivity

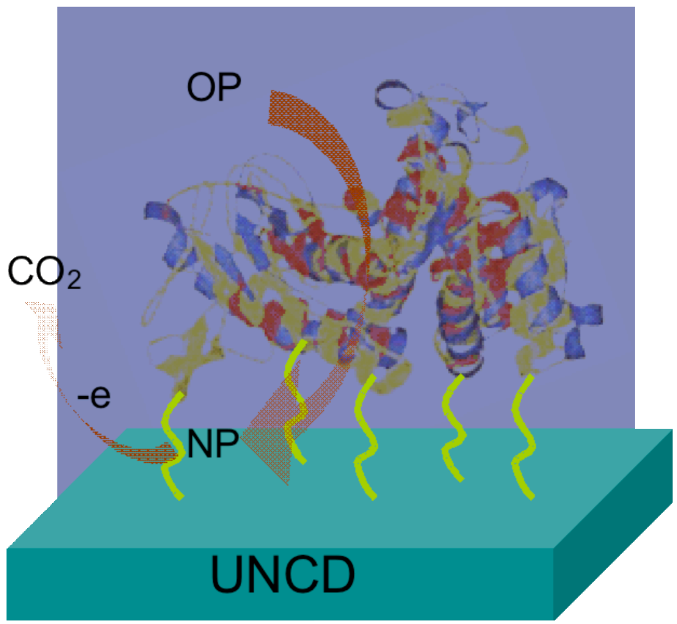






- In-plane motion generated by applied voltage
- Optical out-of-plane detection
- Sensitivity <170 pm/Hz$^{1/2}$
- Characterize dissipation in nanomechanical structures
- Significant applications for motion sensors

Future



- Electrochemical functionalization of carbon surfaces for biosensors
  - How selective is binding?
  - How robust?
- Friction and adhesion studies on tailored carbon surfaces
  - How are friction and adhesion related to the chemistry of the surface?
  - What are the optimal morphological and chemical properties for carbon nanodevices?
- Materials properties studies of carbon materials
  - Thermal conductivity
  - Optimize growth to reduce defects & increase strength
  - Fatigue in carbon MEMS
- Temperature dependent studies of dissipation phenomena in disordered or amorphous carbon
  - Is it possible to identify and characterize dissipating two-state tunneling defects?

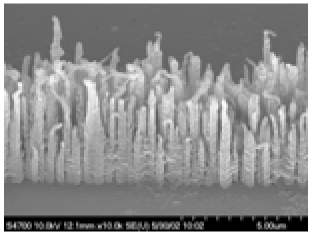
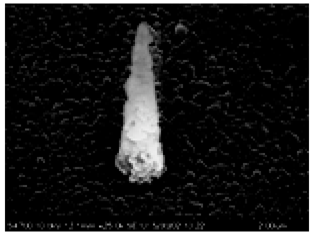
Conclusions

- Glue money is working well
  - New collaborations have been established
  - These collaborations are producing collaborative work
- Demonstrated electrochemical functionalization of UNCD
- UNCD surfaces show tremendous potential for biosensors
- Contact, friction, and adhesion are intimately related to surface morphology and chemistry. H-termination reduces friction in UNCD
- a-D and UNCD have outstanding mechanical properties compared to polysilicon - high strength and toughness.
- New optical measurement technique developed to characterize dissipation in nanomechanical structures.

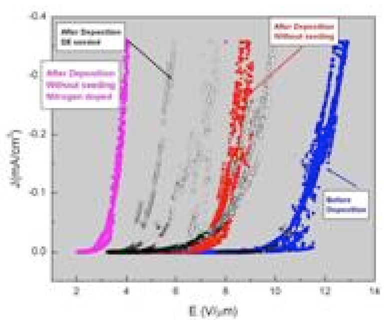
- **Supplemetary Material**
  - **One-page highlights**
  - **Summary of Accomplishments**
    - **Papers, Invited Talks, etc.**

UNCD Related Carbon Nanocomposites

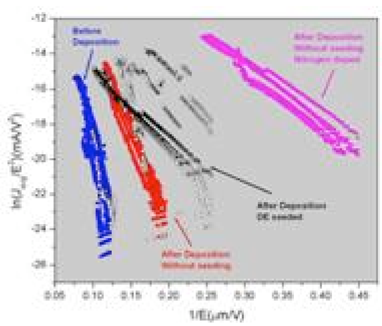
UNCD/CNFs

UNCD can't be deposited on CNFs directly and Diamond seeding layer protected CNFs and also served as nucleation layer for UNCD deposition



I-V characteristics



F-N plot

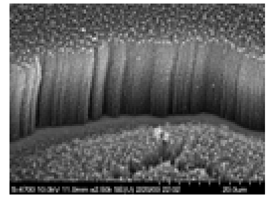
Fowler-Nordheim equation:

$$J = A\beta E^2 / \Phi \exp(B\Phi^{3/2} / \beta E)$$

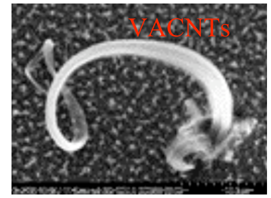
The slope of $\phi^{3/2}/\beta$, represents the combined effect of effective work function and enhancement of local electric field;

$\because$ $\phi^{3/2}/\beta$ ↓ & β ↓ $\therefore$ ϕ ↓ ↓

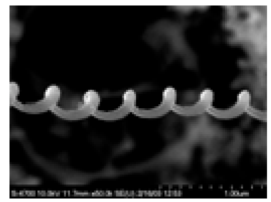
CNTs and UNCD/CNTs



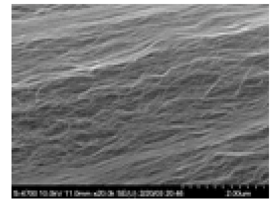
Vertically aligned CNTs



Fast grown CNTs



Coiled CNTs

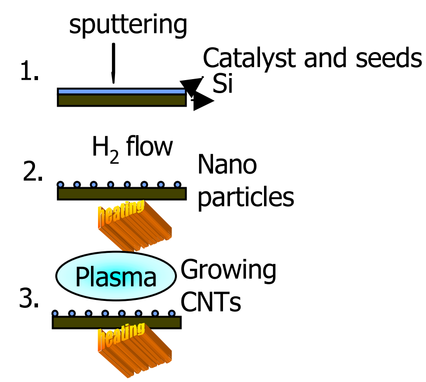


A Bunch of CNTs

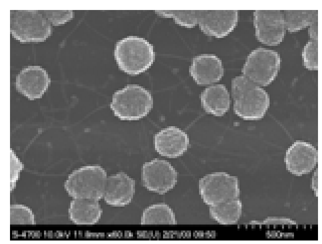
Catalyst: Fe, Ni, Co

Plasma chemistry:

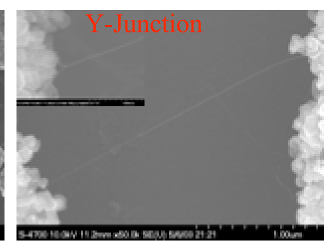
Ar/CH_4;H_2/CH_4; H_2/C_2H_2



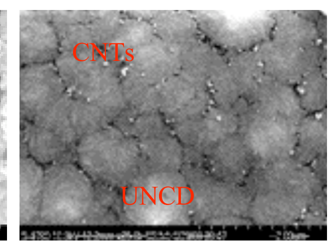
•CNTs and UNCD can be deposited simultaneously. The key is how to address the catalyst for growing CNTs and the seeds for growing UNCD



UNCD/CNTs



CNTs connected pattern



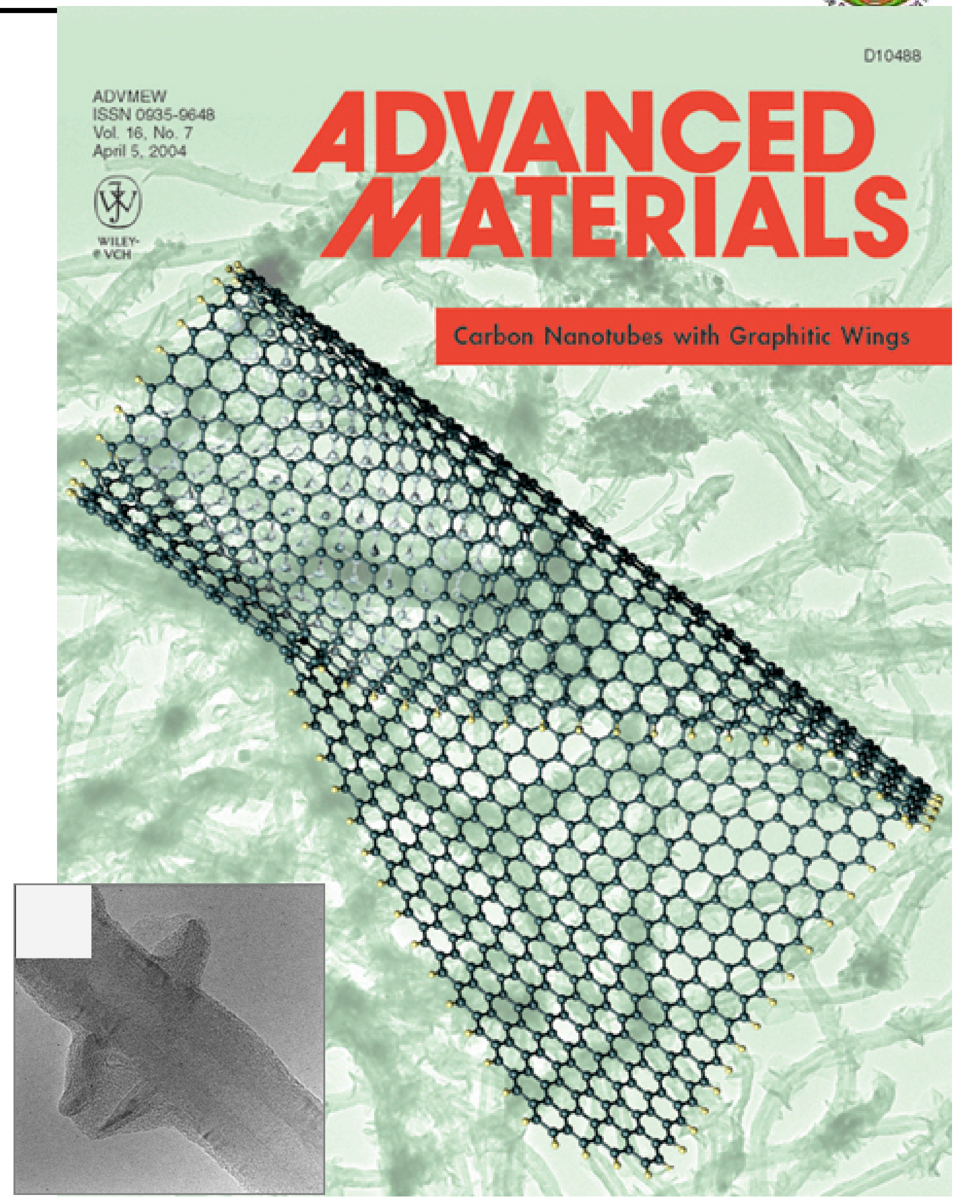
UNCD/CNTs

Each super UNCD particle (randomly distributed) is connected by CNTs, "Self-assembly nanoelectronic circuit" of UNCD and CNTs could be achieved

X. Xiao, J. Elam, O. Auciello, J.A. Carlisle (ANL)

Carbon Nanotubes get their Wings

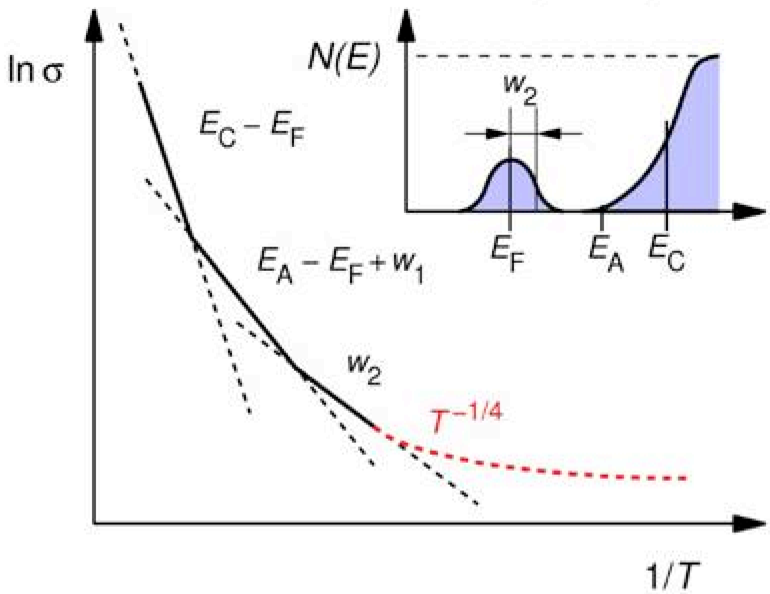
- Carbon Nanotubes were modified using hydrogen-poor Ar/CH4 microwave plasma.
- New carbon nanostructure was created
  - H^+ ions rip open nanotube sidewalls
  - Graphitic sheets are directly grafted onto the nanotube walls.
- Prickly nanotubes have ~2 orders of magnitude more active surface area
- Possible Applications:
  - More senstivice electrochemical electrodes
  - Better biosensors
  - Improved electron field emission
- **Featured on cover of upcoming issue of Advanced Materials [Adv. Mat. 16, 610 (2004)]**



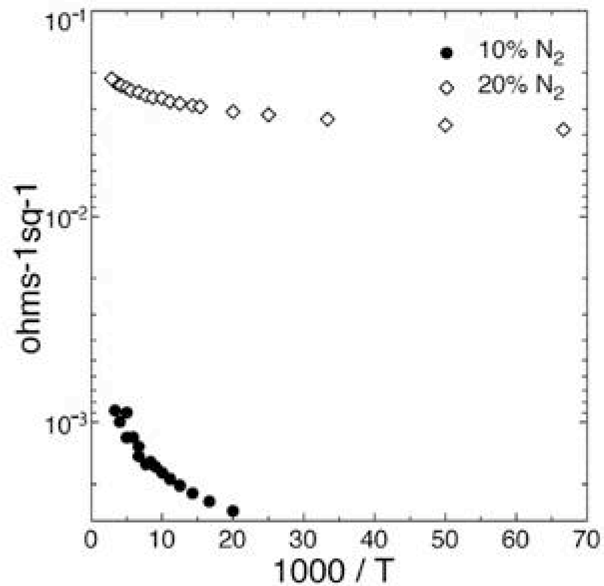
S. Trasobares, J. Birrell, D. Miller, J.A. Carlisle (ANL)
P. Ajayan, O. Stephan (RPI)

Conductivity behaviour of UNCD with temperature

Mott-Davis model (1972)



UNCD Hall measurements

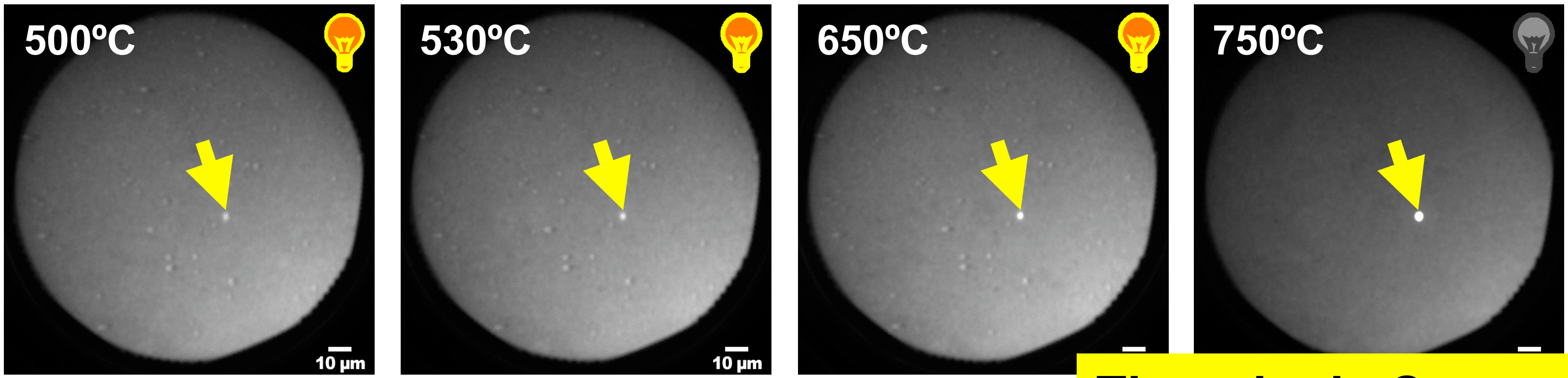


- Low-T signatures of variable-range hopping observed
- Model explains conductivity for *low N concentrations* (GB thicken with higher N content - TODO)

O. Williams, 2003, 2004

Thermionic Field Emission

T- FEEM of S-Doped Nanocrystalline Diamond (50ppm H_2S in H_2)

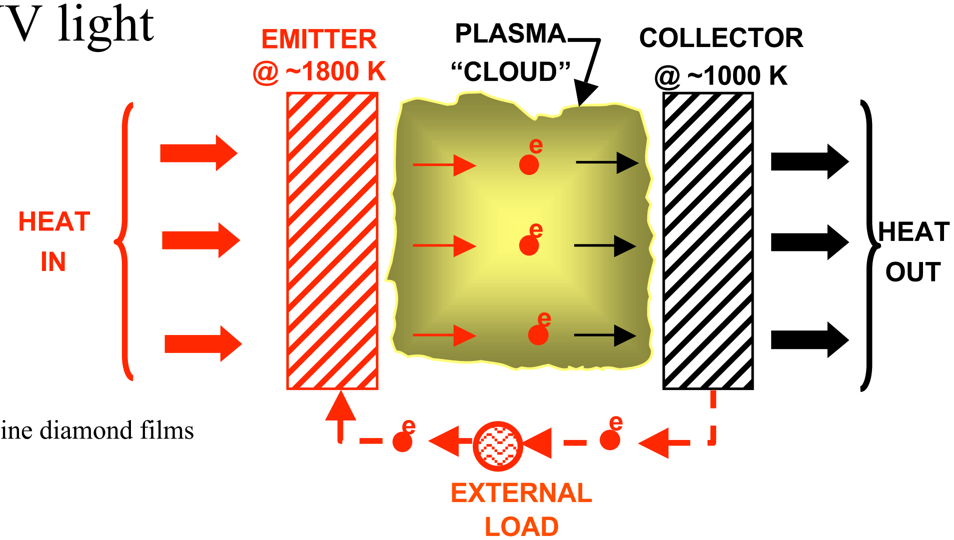


NC STATE UNIVERSITY

with UV light excitation   without UV light

- Electron emission starts at ~XXX°C and increases with increasing temperature.
- Localized emission from singular sites.

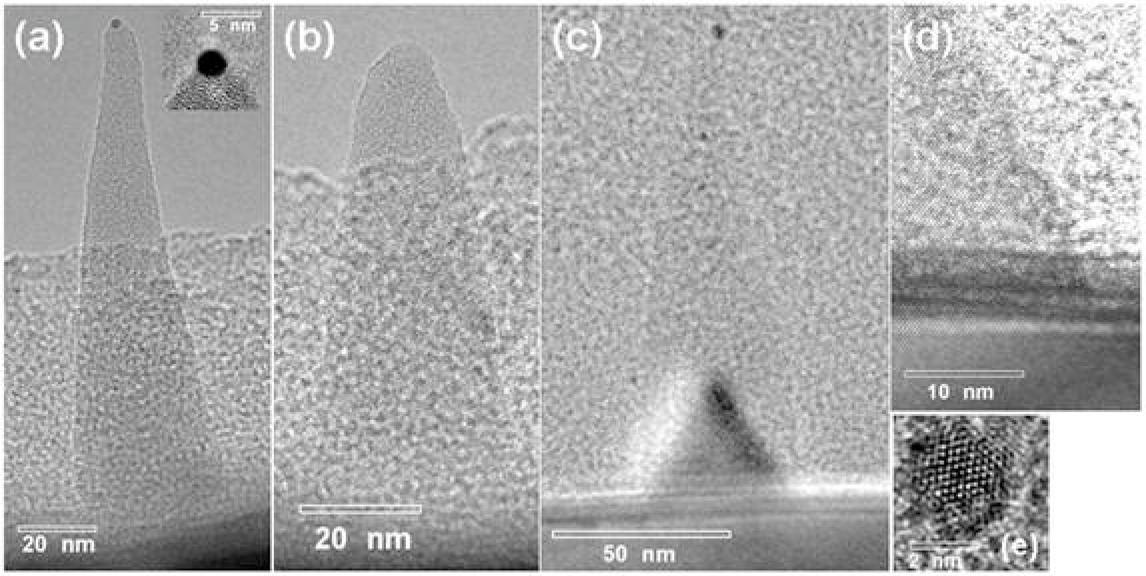
Thermionic Conversion



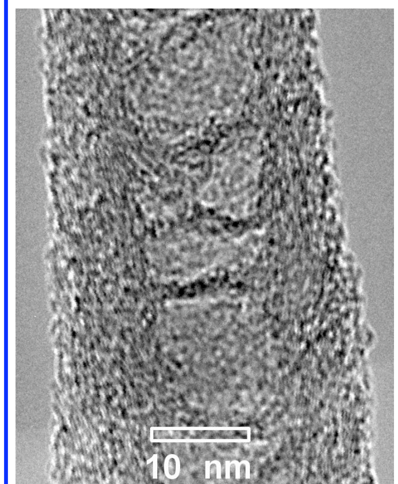
Spatial distribution of electron emission sites for sulfur doped and intrinsic nanocrystalline diamond films
Köck FAM, Garguilo JM, Nemanich RJ, Gupta S, Weiner BR, Morell G
DIAMOND AND RELATED MATERIALS 12 (3-7): 474-480 2003

HRTEM: internal structure of the nanocones

Nanocone

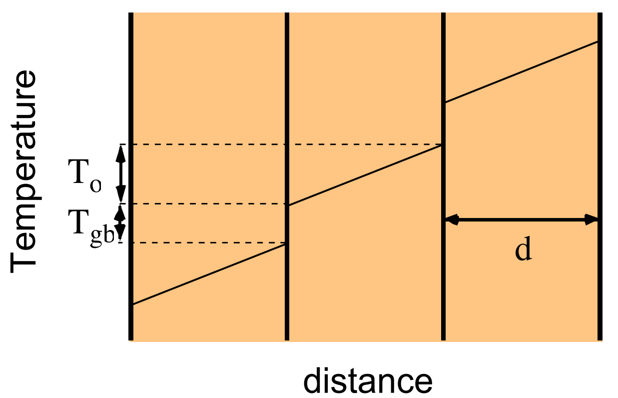


VACNF



- Catalyst particle located at the tip (tip growth mode)
- Amorphous structure
- Silicon cone formed at base is continuous with the substrate
- Rounded tip due to plasma etching if catalyst particle is lost: seen (b)

Thermal Transport and Phonon Scattering at Diamond Interfaces



- Kapitza resistance results in temperature discontinuities at interfaces

Schelling, Phillpot and Keblinski, JAP 95, 6082 (2004).